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## A Study of Undercooling Behavior of Immiscible Metal Alloys in the Absence of Crucible-Induced Nucleation

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The purpose of this study is to investigate the question: Would eliminating the crucible eliminate the wall-induced nucleation of one of the liquid phases in an immiscible alloy and result in undercooling of the liquid into the metastable region thereby producing significant differences in the separation process and the microstructure upon solidification. Another primary objective of this research is to study systems with a metastable miscibility gap and to directly determine the metastable liquid miscibility gap by undercooling experiments. Nucleation and growth of droplets in these undercooled metallic liquid-liquid mixtures is also being studied.

An equilibrium liquid immiscible system, Ti-Ce, was chosen for study across its miscibility gap. The Ti-Ce (46.6 to 92.0 w/o Ce) system was chosen after consideration of a number of factors including an immiscibility dome having a high enough temperature to allow a sample (with a reasonable diameter of 5mm) to totally solidify during its free-fall, vapor pressure at the critical temperature, oxygen affinity, reliable phase diagram, and toxicity. The MSFC 105-meter Drop Tube facility was used to provide a low-gravity and containerless environment during cooling and solidification. One-gravity experiments were performed in an electromagnetic (EM) levitation coil in the belljar of the Drop Tube. Container effects on the wetting ability of the different phases is or has been extensively studied elsewhere, but not necessarily for the nucleation and undercooling effects.

Results of this investigation indicate that containerless processing of immiscibles may not promote the undercooling of the single-phase liquid into the metastable region. Although no recalescence event was observed for this liquid-liquid transition (possibly because the enthalpy released during this transition was lower than the limits of our detectability), undercooling did occur across the miscibility gap for the solidification of the Ti phase that eventually separated. In every undercooled sample, massive separation of the liquid phases had occurred. Metallurgical analysis of samples undercooled in unit-gravity showed signs of vigorous convective stirring and shearing by the EM field of the L1 Ti-liquid into several large globules. In almost every low-gravity processed sample, the L1 liquid formed the near-concentric sphere within a Ce shell with some residual smaller spherical particles dispersed throughout the Ce. This configuration is predicted from surface energy minimization by the lower surface energy (Ce) component and from Marangoni convection via the inward temperature gradient.

Plots of both the melting and solidification or maximum recalescence temperatures indicate that the monotectic temperature is 1815(10 K rather than the 1720 K temperature commonly accepted. Wavelength-dispersive spectroscopy (WDS) confirmed the

equilibrium concentrations within the phases as depicted in the metallographs. WDS also showed some cerium oxide precipitates but no perceptible oxygen within the Ce or Ti phases. Based on this and the fact that the  $\text{CeO}_2$  precipitates are the limiting molecular-form for oxygen solubility in Ce, the higher monotectic temperature reported here is probably not the result of a tertiary oxygen constituent. Crucible studies of the binoidal and monotectic points are just beginning.

High undercooling can induce not only various solidification pathways, but also a precursor reaction, e.g. liquid separation. However, the latter effect of undercooling has not yet been studied extensively. Several Cu-refractory alloys such as Cu-Co, Cu-Fe and Cu-Nb, which are of considerable technological importance, possess a flattened liquidus implying a thermodynamic tendency to immiscibility upon undercooling (T). Previous papers have shown the metastable liquid miscibility gap (MLMG) and microstructural transition from dendrites to droplets for the former two systems. However, the early studies suffered from either oxidation or electromagnetic stirring. Furthermore, there have been few reports on direct measurement of the MLMG, which may defy correlation between the metastable demixing and undercooling. Also little information is available about the formation and coarsening of droplets in a metallic liquid-liquid system, which is essential to understand melt separation process in undercooled regimes. The Cu-Nb phase diagram has been under active debate for more than three decades; thus a corroboratory experimental study is needed with the purpose of defining the correct phase diagram.

In this study, the melts of Cu-Co, Cu-Fe and Cu-Nb alloys were processed in a container and containerless state respectively in order to determine separation temperatures and liquidus temperatures, and to investigate the effects of undercooling, concentration, cooling rate, electromagnetic stirring, and impurities on the microstructure. Results include direct measurement of liquid separation, phase diagram determination, and microstructural analysis.